

ART. IX.—*Some Remarks on the Crude Sodas of Commerce*; by JOHN REVERE, M. D. *Lecturer on Chemistry, applied to the Arts, at the Maryland Institute for the promotion of the Arts and Manufactures.*

TO THE EDITOR.

New York, October 15, 1827.

Sir—In a course of lectures on chemistry, applied to the arts, I had occasion to collect the facts contained in the following paper. To those who are familiar with the science of chemistry, there will be little that is new. I have been induced to offer these remarks to your Journal, rather from its title, than the general scope of its contents, which I observe are almost purely scientific.* The importance of this substance in the useful arts, the ignorance observed among manufacturers and dealers respecting its nature, and the shameful impositions sometimes practised, constitute its chief claim to your attention. The facts stated may be relied upon, as they have been established by repeated experiments.

JOHN REVERE, M. D.

Crude soda, in whatever manner procured, is generally known in this country, among manufacturers and merchants, by the name of *barilla*. But as the value of the article depends very much upon the former circumstance, it will be proper to observe, that it is obtained as an article of merchandize, chiefly in four different modes, viz. 1, in a saline form, on the surface of the earth, and from the water of certain lakes; 2, from the incineration of certain land plants; 3, from the combustion of marine plants; and 4, from the decomposition of sea salt by chemical processes.

The crude soda, formerly known by the name of *natron*, is found in considerable quantities in Egypt, the interior of Africa, and in South America. It exists in lakes, and in particular districts, and forms an efflorescence upon the surface of the earth during the dry season. I am not aware that in this form, it is known as an article of commerce, in the United States.

The most valuable of the crude sodas known in this country, are obtained by the incineration of several kinds of

* The Editor would be happy to receive more communications on the *Arts*, while he would not wish to lower the character of this Journal for *Science*.

plants, which grow in the vicinity of the sea. The best is brought from Alicant, Malaga, and Carthagena, in Spain; it is obtained from an annual plant, the *salsola sativa*, which is cultivated and cured like hay, and afterwards burnt in holes dug in the earth. From the great quantity of soda it contains, it melts into thick paste, which on cooling, becomes condensed into a stonelike mass; the popular name of this plant in Spain, is *barilla*. So highly is this plant esteemed in Spain, that, according to Mr. Parkes, the exportation of the seed is prohibited, under penalty of death. There are several varieties of the *salsola* cultivated on the shores of the Mediterranean, especially in the island of Sicily, and also in the Canary Isles, which yield an abundance of soda. For convenience, all the crude sodas obtained by the combustion of land plants, may be called *barilla*. The *barilla* most common in our market is brought from Spain, Sicily and Teneriffe. Although many parts of the United States are favorably situated, I have known but one attempt to cultivate them. It was made on the eastern shore of Maryland, from seed procured for the purpose in Sicily. The attempt failed, owing evidently to the imperfection of the seed.

The increased demand for soda for the arts throughout the civilized world, has led men to seek other sources from which this useful substance may be procured. Modern science and industry have succeeded in extracting a large supply from marine plants, which were accounted so entirely worthless among the ancients, that *algâ projectâ vilior* was a common proverb at Rome. The substance procured by the combustion of these plants is called by the French *varech*, and by the English *kelp*. The inhabitants of the coast of Europe have been in the habit, from time immemorial, of collecting the *sea weed*, *wrack* or *sea ware*, as it is indiscriminately called in Great Britain, and manufacturing it into a coarse alkali, for domestic purposes. It is only, however, within a century that any attempt has been made in Great Britain to prepare the kelp in a large way. It was in the year 1723 that this substance was first brought into the market as an article of merchandize. But the great consumption of the alkalies in the modern arts, especially by the bleacher, soap and glass manufacturer, and other manufacturing chemists, has attracted more and more attention to the subject, until the manufacture of kelp in Great Britain has become a very important department of industry. I am under the impression that kelp has never been brought into our market, or attempted to

be manufactured in the United States, but as it appears to me that this manufacture may be introduced advantageously among us, I propose to give some account of the most approved method at present practised, in the hope that it may direct the attention of those persons to the subject, who are conveniently situated for making the attempt. From the increase of our manufactures, and as all the crude sodas at present consumed are imported, it is highly probable that there would be a full demand for the article. The material may, for the trouble of collecting it, be had, in immense quantities, along our extensive sea coast, nor can any thing be cheaper or more simple than its manufacture. Some idea may be formed of the advantages that may be derived from this manufacture, from the great and obviously increasing importance that is attached to the subject in Great Britain. There are frequent communications on the subject in their best journals, and prizes offered to encourage its cultivation, by their societies for the promotion of the arts and manufactures. As long ago as 1798, it was stated by Prof. Jameson in his Mineralogy of the Shetland Isles, that "farms which before the introduction of kelp rented at forty pounds, now rent for three hundred pounds." It is also asserted by Mr. Parkes that Lord McDonald of the Isles, now realizes ten thousand pounds per annum from his kelp shores, which his ancestors considered valueless.

Nearly all marine plants, especially the *fuci*, are found to yield soda from combustion. Those which are preferred are the *fucus vesiculosus*, *nodosus*, and *serratus* ;* they are found spontaneously growing on the rocks near the shore, generally between high and low water marks. Generally speaking, bays and caves that are sheltered from the winds and tides are found best, though some of the *fuci* flourish best in the most exposed situations, and the strongest tideways. Formerly, the kelp was made entirely from the floating sea ware, as it washed up on the shore, but, since the manufacture has become profitable, greater care is taken in its preparation. It is now common to cultivate these plants by depositing on sandy beaches, large boulder stones, to which the *fuci* may readily attach themselves, and to cut and collect the ware ; colcareous stones are found best. In the Repertory of Arts,

* It would appear that this class of plants has not received much attention from botanists in this country. I have been informed, however, by good authority, that these *fuci* are found in abundance along our coast.

there is a particular description of the process employed in the manufacture of one hundred and fifteen tons, on the farm of Stroud in Horris, which received the prize of the Highland Society.

This sold for five pounds ten shillings per ton. As this is considered the most approved method, I will give an abstract of it. In the Orkneys, they account the spring the best season for cutting the ware, because they are then less exposed to the rains. The weeds that are left bare by the tide are cut with sickles, and those under water with bill hooks. It is considered important to land the ware, as fast as it is cut, and to carry it to a suitable situation to dry; it is thought that as soon as the weed begins to wilt, the pores of the plant become relaxed, and allow the soda to exude, which is dissolved and lost, if the ware be left in the water or exposed to the rains. There is no doubt that kelp made from such ware is weaker. It is spread on clean ground to dry, and, when pretty well dried, it is collected into large cocks, protected from the rain if possible, and allowed to heat for six or eight days, or even from fifteen to twenty if the ware has been collected from coves with muddy bottoms.—A dry day, when there is a brisk breeze, is selected for burning the ware, which is conducted in the following manner. The kilns are rudely constructed of stones and turf upon the firmest sward that can be found. The most convenient are about two feet six inches in height, two feet four inches in breadth, and from eight to eighteen feet in length, according to the quantity of ware to be consumed. A little dry straw is first spread over the bottom of the kiln, and kindled, to which the ware is slowly added, as fast as it is consumed, the combustion being accelerated by the breeze. Should the weather become calm, or if the ware is not sufficiently dry, the ashes cool and cake into white crusts, when it becomes necessary to rake the ashes until the combustion is perfect, before adding fresh ware. When the ware is all burnt, the last process consists in working or raking the ashes with iron rakes, so that the combustion of every part shall be perfect. It is transformed into a thick paste, which, on cooling, becomes solid, somewhat resembling good indigo; it is then broken up into masses of about two hundred weight, covered with dry ware, and is ready for the market. If the ware has been taken from a muddy situation, it sometimes happens that the ashes remain dry, and do not

assume the form of a paste. By allowing the combustion to continue a little longer, or by adding some salt or saltpetre, the difficulty is easily overcome. The kelp is found to yield from three to six or eight per cent. of pure soda.

France was in the habit of depending principally upon foreign countries, for the supply of crude sodas, until the period of the revolution. In consequence of the wars lighted up by that event, she found herself cut off from the rest of Europe, and compelled either to abandon some of her most important manufactures, or to find within herself the means of supplying the raw materials. She was entirely destitute of many articles of daily, and indispensable use. Surrounded by enemies, she had not even the means of obtaining nitre for preparing gun powder for her armies. This state of things, and the great political excitement that existed at the time, resulted in prodigious and successful efforts, to supply herself from sources which had not before been thought of. The value of the physical sciences under these circumstances was perceived, nor is there perhaps a period in their history more honorable than this. No longer confining herself to the closet and laboratory, philosophy went forth, and relieved with her treasures, the distresses of the state. In the enthusiasm of the moment, the usual motives of human action seemed suspended; especially among men of science, every thing like private interest seemed lost sight of, in a desire to promote the public good. Important discoveries in the arts, which if practised in secret must have yielded immense emolument, were freely promulgated for the good of the republic. In this honorable competition of the sciences, chemistry stood pre-eminent. The most eminent chemists in France, were formed into committees, by the committee of public safety; the results of their investigations will be found in the early volumes of the *Annales de Chimie*, forming the most valuable series of papers on chemistry, applied to the arts, that can perhaps be found in the history of the sciences.

Among the most important of these papers is the report of Messrs. Lelievre, Pelletier, d'Arcet, and Girard, on the best means of extracting soda from sea salt. This led to the extensive manufactory of artificial soda in France, which is at present, not only principally employed in their own manufactories, but has become a considerable article of export. The process recommended by the committee, and which

with some modifications, is still practised, was invented by Messrs. Leblanc and Dizé. The process is briefly this,—it consists in decomposing the muriate of soda, by sulphuric acid. The sulphate of soda, thus formed, is intimately united, in certain proportions, with charcoal and chalk pulverized. By the application of a suitable temperature, in a reverberatory furnace, a somewhat complicated series of chemical changes takes place. It has been supposed that sulphate of soda is decomposed, a part of the sulphur of the sulphuric acid, being consumed in the form of sulphuretted hydrogen, forms slight explosions, and exhibits the appearance of fire works, while the unconsumed sulphur, remains in combination with a portion of soda and lime, forming hydro-sulphurets, sulphates and sulphites. In the meanwhile, the carbonic acid of the lime, and that formed by the combustion of the charcoal, unite with the soda, and form the carbonate of soda. This part of the process, requires considerable tact in its management, as the value of the article depends upon the completeness of the decomposition of the sulphate of soda, and the quantity of carbonate of soda that is formed. The process lasts about seven hours, and the residuum, thus obtained, resembles in its appearance fine barilla.*

A considerable quantity of the artificial barilla, has been imported into the United States. In consequence however, of the badness of the article in some instances, but especially from the quantity of sulphur, that even the best contains, it is entirely fallen into disrepute. So little is it esteemed in this market, that the soap makers, who are the principal consumers, as several of them have declared to me, would not accept the article as a present, though they are sensible that it contains a large proportion of alkali. They find the ley, obtained by the lixiviation of the artificial barilla, contains so much sulphur, that when boiled and mixed with the other materials for making soap, the quantity of sulphuretted hydrogen disengaged, is so great, as to render the works almost untenable, while the soap becomes of a dirty blue color, and is rendered unsaleable.

Knowing that this substance is generally employed in the soap manufactories of Marseilles, and that these inconveniences are not complained of there, I was induced to enquire

* For a particular account of the process, see *Ann. de Chim.* v. 19.

into the cause of this, in order to ascertain, whether the evil complained of by our manufacturers, might not be remedied. My attention was naturally first directed to the difference of the two manufactories; the following are the principal points of difference. In France, soap is generally made from soda and olive oil; it is colored, and that most sought after is called *bleu pâle*. In this country, we generally use the animal oils, and in all but the very fine soaps, our manufacturers are in the habit of using a considerable proportion of rosin; the most saleable of this kind of soap, is of a bright yellow color. In France, the soap is marbled, by adding to it while in a mass, a solution of green vitriol, sulphate of iron. Now it appears, from the statement of M. Laurens, who is practically acquainted with the subject,* that in order to impart to the soap the precise tint, so much sought after, the *bleu pâle*, the presence of the sulphuretted hydrogen, or rather of the alkaline hydrosulphuret, (for both of the alkalis are found to answer the purpose,) is indispensable. In this process, the sulphuretted hydrogen, when united with the iron and oil, imparts a greenish blue color, which does not combine with the soap, but is dispersed through it, during ebullition, in small masses, so as to produce the marbled appearance. M. Laurens remarks, that the more scientific manufacturers at Marseilles, are in the habit of adding sulphuretted hydrogen, after treating the soap with the green vitriol, should it not be found to possess the proper color. This seems to afford a ready, and natural solution of the fact, that artificial barilla is used with advantage in the soap manufactories of France, while in this country it is so objectionable. I have had recourse to a number of experiments with different substances, for the purpose of devising a cheap method of getting rid of the sulphur, combined with artificial soda, so inconvenient to our soap makers, but without arriving at any very satisfactory results. Some advantage may be obtained if the ley be introduced into open vats, into which the clippings of tin plate, or iron have been thrown, and left standing exposed to the air, for several days, and occasionally agitated.

Economy of materials is the basis of successful manufacturing, and, as the intrinsic value of the crude sodas depends entirely upon the quantity of pure alkali they contain, the

* See Ann. de Chim. v. 67.

manufacturer should be able to form a correct judgment in this respect. For this however, our dealers and manufacturers have a very inadequate standard—they depend almost exclusively on the senses, and the history of the article. The appearance, taste, and weight are their chief guides; after a long experience, and having paid dearly for that experience, no doubt they can form some general idea of the value of the article, but after all, their judgment, thus formed, must be loose. They generally break a piece of the barilla, and apply the tongue to the fracture; if the soda be in a caustic state, even though in small quantity, it will excite a much stronger sensation of taste, than when it exists in larger quantity, in the form of a carbonate. Nor is the history of the article more to be relied on, as there are several different qualities brought from the same market. Indeed I have known some instances in which the most experienced soap manufacturers, and even large manufacturing chemists, have been most egregiously deceived, by judging of the article in this loose way. I lately assayed a sample of artificial barilla, that was sold at eighty dollars per ton, the price of the best in which there was scarcely an appreciable quantity of soda, while a sample of Alicant barilla, yielded fifty eight per cent. of pure soda.

There are a great number of methods, recommended for assaying the crude sodas. An exact assay is undoubtedly, a very nice and even difficult operation, but with a little attention, any manufacturer may make a sufficient approximation for all practical purposes. I have tried several, but would recommend the following as the best; it is with some modification, the one recommended by Mr. Parkes.

Take a quantity of diluted sulphuric acid, say six parts of water to one of the sulphuric acid of the shops; this will be of a convenient strength, and will be found about the specific gravity of 1.100. Select a phial that pours and drops well; it should have a glass stopper with a score running lengthwise along it, and that fits accurately, so that we may be able exactly to fill the phial. With good scales, using a counterpoise for the phial, we should carefully ascertain the precise number of grains of the diluted acid that the bottle will contain. Lastly, we must ascertain with nicety the number of grains of the diluted acid that is required to saturate one hundred grains of *pure* soda. Having made these preparations, we may at any time, in the course of a few hours, de-

termine the quality of a lot of barilla. We select a number of fragments, which may be considered as a fair sample of the whole; pulverize them finely in an iron mortar, and then weigh out two or three portions of one hundred grains each, which may be put in as many tumblers, together with about two or three ounces of water; distilled water is best. After it has stood for a few hours, being occasionally stirred with a glass rod, carefully strain off the solution into a clean tumbler, through bibulous paper. Wash the residuum by adding small quantities of water until it passes through the paper tasteless. Add a solution of litmus until the alkaline solution becomes decidedly blue. Having then filled the phial exactly with the diluted sulphuric acid, in order to observe the change of color more accurately, place the tumbler containing the alkaline solution, upon a sheet of clean white paper; and then pour the acid in slowly and at intervals, agitating at the same time with a glass rod, until the litmus begins to assume a red color. We must now proceed still more slowly and carefully; the redness is at first faint and delicate, and is produced by the carbonic acid gas evolved and not by the sulphuric acid. On first adding the sulphuric acid, no effervescence is observed; probably because the first portions of acid combine with that part of the soda that remains in a caustic state. When the whole of the soda is saturated, this will be indicated by the marked deeper red color, and by the acid forming but a mechanical mixture with the solution, as it is added drop by drop, without any chemical action. By weighing the diluted acid remaining in the phial, we can determine how much has been consumed in saturating the alkali; and, as we already know the number of grains of the diluted acid, required to saturate one hundred grains of pure soda, by the rule of proportion we can at once ascertain the proportion of pure alkali in the barilla. By repeating this operation with the two remaining portions, we can make a still closer approximation to the truth.

But this process, which is found to answer very well in assaying barilla and kelp, is an insufficient guide for ascertaining the quality of the artificial soda, especially when indifferently manufactured. This always contains a quantity of the hypo-sulphite and hydro-sulphuret of soda, which are decomposed by, and assist in saturating the sulphuric acid, and thus give a too high return of the quantity of alkali; especially as these substances are positively injurious in the man-

ufacture of soap, as pursued in this country. This difficulty, however, may be obviated, by the following process, recommended by Welter and Gay Lussac.—Mix a little of the oxy-muriate (chlorate) of potass with the sample of crude soda to be tried, and expose the mixture to a low red heat; a platina crucible is recommended by them—but one of silver or porcelain will answer, if the process is carefully pursued; the latter was used by myself for the purpose. The sulphurets and sulphites are thus converted into sulphates, and the oxy-muriate into neutral muriate. After this process, the artificial soda may be assayed in the manner above described.

I shall close this paper, which has already extended much farther than was at first intended, by a few remarks on a point, in which I find there are very mistaken views entertained by the dealers in the crude sodas. It is a common opinion, that barilla that is broken into small fragments and powder has lost its strength; on this account there is generally an allowance made in the sale of the article, of from ten to fifty per cent. for this part of the barilla. This opinion, however, is true only to a very limited extent. A considerable part of the soda is at first in a caustic state; that part of the mass, therefore, that is exposed to the air, imbibes carbonic acid gas and moisture, but, unless the barilla has been wet, and thus lost a portion of its alkali, it is diminished in value only by the additional weight of the carbonic acid gas and humidity it may thus have acquired.
